Partitioning of Non-ionic Surfactants Between CO_2 and Brine

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Abstract: The partitioning of non-ionic surfactants in a CO_2/synthetic brine system was studied for a selection of surfactants at reservoir conditions for CO_2 enhanced oil recovery and aquifer storage. Alkyl and alkylphenol ethoxylates with different degrees of branching in their hydrophobic moiety were chosen. Generally, higher temperature and pressure promoted increased solubility in CO_2. Branching of the hydrophobic moiety tends to favour CO_2 solubility (higher partition coefficient). Highly branched moieties were found to hinder solubility probably due to a decrease of their conformational entropy. The addition of an aromatic ring connecting the ethoxylate moiety and the hydrophobic moiety seemed to have an adverse effect at lower temperatures. For two surfactants, the effect of concentration on partitioning was also studied. The partition coefficient decreased for increasing concentrations until a plateau was reached above the corresponding surfactant critical micelle concentration (CMC). This may indicate micelle formation both in the CO_2 and in the aqueous phase.

Keywords: Mobility control of CO_2, foam, enhanced oil recovery, aquifer storage, surfactant partitioning

1. Introduction

CO_2 is becoming a prominent solvent for different applications. Its foams and emulsions with water are of interest due to its potential for various applications (Johnston and Rocha, 2009). Two large scale applications are enhanced oil recovery (EOR) and subsurface sequestration. However, these methods encounter various technical challenges. The relatively low density and low viscosity of CO_2 can lead to gravity segregation and viscous fingering giving early CO_2 breakthrough and poor volumetric sweep efficiency. The result of this may be low oil recovery (in EOR) and reduced utilisation of the storage capacity (in CO_2 sequestration) (Solbakken *et al.*, 2013; Tsau and Grigg, 1997).

Early breakthrough can be counteracted by decreasing the mobility of the CO_2. This can be achieved by increasing the viscosity using additives to the CO_2 or by dispersing the CO_2 into another fluid (brine). It is not easy to increase CO_2 viscosity. The additives (direct thickeners) must solubilize in CO_2 and provide self-interactions that can give the desired viscosity enhancement. During decades efforts have been made trying to find suitable additives (Enick *et al.*, 2012). However, the best CO_2 additives found are not practical due to their high costs and detrimental environmental impact.

The second method for decreasing CO_2 mobility is through creating dispersed systems. CO_2-in-brine dispersions (hereafter called foams) may have high apparent viscosities depending on the surfactant used. Foams can also be formed and stabilized by nanoparticles. Even though nanoparticles adsorb more strongly at interfaces, larger energy input is required to form foam. This criterion is not met at reservoir flow velocities which typically do not exceed few feet/day (except close to injection wells) (Binks, 2002; Espinosa *et al.*, 2010; San *et al.*, 2016; Yu *et al.*, 2012).

Surfactant-stabilized foam is so far the most promising CO_2 mobility reduction method. However, this also faces several challenges. One potential problem is the presence of oil which may destabilize foam through different mechanisms including spreading and entering phenomena (Manlowe and Radke, 1990; Schramm and Novosad, 1990; Wasan *et al.*, 1994). However, the sensitivity of foam to oil may have

both advantageous and disadvantageous consequences. During miscible CO_2 flooding, the foam may be more stable in pores where the oil has already been displaced helping to divert CO_2 within the reservoir to places where the oil is not displaced. There, the lamella will collapse and release CO_2 in the CO_2/oil front. On the other hand, if the stability of the foam is sensitive to minute oil residues it can have an adverse impact on foam propagation (Vassenden *et al.*, 2000).

Another challenge to face during surfactant-stabilized foam flooding is surfactant depletion due to adsorption on the pore walls of the reservoir rock. The adsorption will be determined by the pore wall mineralogy and charge, type of surfactant, pH, temperature, ionic strength, electrolyte concentration (Bera *et al.*, 2013; Curbelo *et al.*, 2007). In traditional foam technology, the surfactant is transported in the denser water phase. At some distance from the injection well, the surfactant solution and CO_2 will segregate and foam cannot be formed. If the surfactant is transported in the CO_2, foam may be formed wherever gas and water coexist.

Mobility control can also be beneficial for aquifer storage of CO_2. In order to increase the storage capacity and to avoid excessive build-up of pressure, formation water must be produced from the formation. The total storage capacity of a formation can be significantly increased if the volumetric sweep is improved. This can reduce the total storage cost if low-cost CO_2 soluble surfactants giving suitable mobility control at low flow rates can be identified (Grimstad *et al.*, 2018).

Efforts for finding and developing CO_2 soluble surfactants have been made since early 1990. The first effective surfactant developed was fluorinated (Hoefling *et al.*, 1991). These types of surfactants are impractical due to their environmental impact and high costs. Since then, the effort has been focused on finding non-fluorinated surfactants. Due to the amphiphilic nature of surfactants, CO_2-soluble surfactants will also dissolve in the aqueous phase and thus, partition between both phases. CO_2 solubility and partitioning has been studied for several surfactant types such as dioctyl sodium sulfosuccinates (AOT) (Le *et al.*, 2008), linear and branched alkylphenol ethoxylates (McLendon *et al.*, 2012; Xing *et al.*, 2010), branched alkyl ethoxylates (Xing *et al.*, 2012), ethoxylated cocoamines (Chen *et al.*, 2012) and triblock copolymer surfactants (Adkins *et al.*, 2010).

However, the partition and solubility studies reported in the literature only give values for specific temperatures, pressures and surfactant concentrations, and it is difficult to find data on how the partitioning is influenced by changes in these variables for CO_2-brine systems.

Injection of surfactant through the CO_2 phase was introduced by Le *et al.* with promising core flooding results. With this novel injection strategy, the surfactant dissolved in the CO_2 phase will partition to the formation brine and foam can be formed in-situ, obtaining a delayed CO_2 breakthrough and an increased oil recovery (Le *et al.*, 2008).

Knowing how partitioning is affected by pressure and temperature is important for foam flooding since the mobility and strength of the foam depends on the surfactant concentration, which depends on surfactant adsorption onto rock and partitioning between the phases (Ashoori *et al.*, 2009). Partitioning of surfactant and its concentration dependence are therefore important input data for a foam simulator.

The objective of the current work was to determine the CO_2 partition coefficients in CO_2-brine systems for a selection of commercially available non-ionic surfactants at variable pressures and temperatures relevant for CO_2 enhanced oil recovery and CO_2 aquifer storage on the Norwegian Continental Shelf. The dependence of CO_2 partitioning with varying surfactant concentration was also addressed.

2. Materials and Methods

2.1. Gas

The CO_2 was obtained by AGA A.S. (99.7 %).

2.2. Synthetic seawater

The synthetic seawater (SSW) composition used in this study is shown in Table 1. The SSW was filtered through 0.45 μm cellulose nitrate filters.

Table 1. Synthetic seawater composition.

Salt	Conc. [g/l]
NaCl	23.612
$CaCl_2 \cdot 2H_2O$	1.911
$MgCl_2 \cdot 6H_2O$	9.149
KCl	0.746
Na_2SO_4	3.407

2.3. Surfactants

A selection of non-ionic surfactants was chosen for the CO_2 partitioning studies. The surfactants were divided into two groups, alkyl ethoxylates and alkylphenol ethoxylates. Each group had hydrophobic tails ranging from linear to highly branched alkyl groups. The surfactant chemical structures used are described in Figure 1.

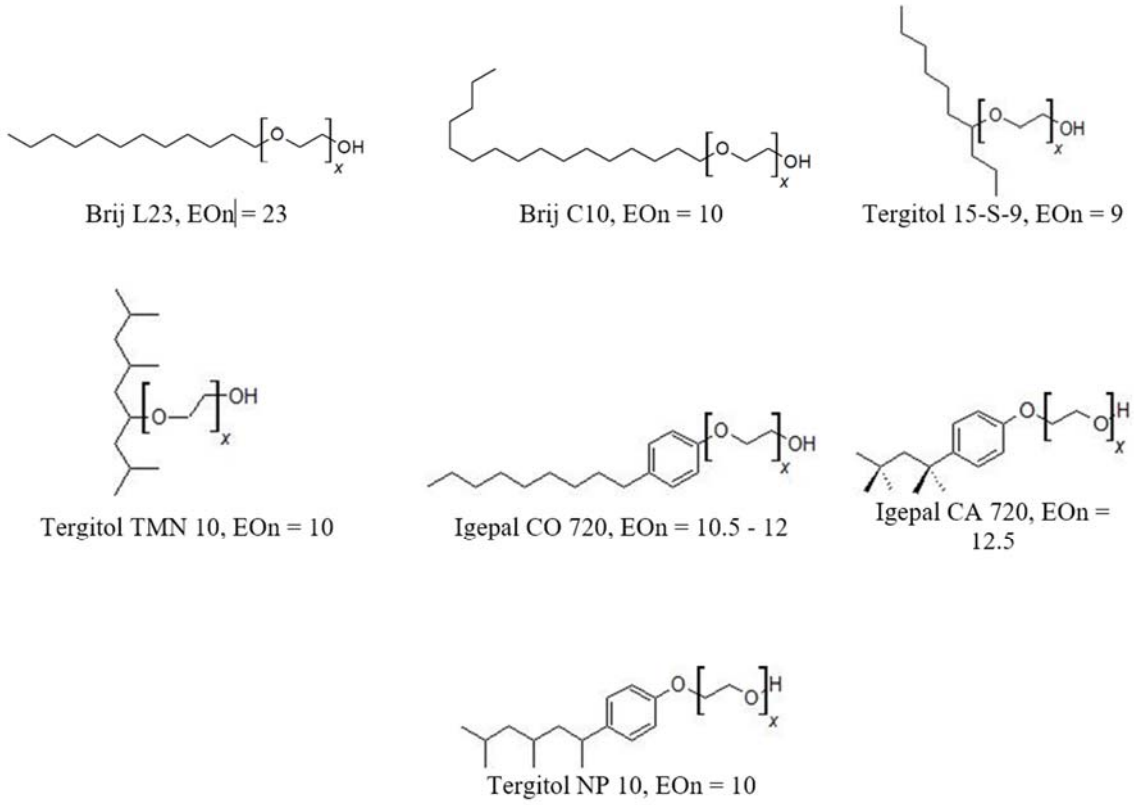

Figure 1. Surfactant chemical structures (EOn symbolizes the average number of ethoxy groups).

All surfactants were obtained from Sigma-Aldrich with a concentration of 100 wt.% of active material except for Tergitol TMN 10, which was obtained with a concentration of 90 wt. % of active material.

3. Experimental

3.1. Cloud point determination

0.5 wt.% surfactant in SSW was placed in a water bath equipped with a temperature controller. The temperature of the water bath was slowly increased using small increments until the cloud point of each solution was observed.

3.2. Measurement of surfactant partitioning

Measurements of surfactant partitioning were performed in a high-pressure high-temperature pVT-cell with an internal piston for pressure/volume control (DB Robinson). The cell temperature was controlled by a heating cabinet with circulating air. A volume of 15 ml of aqueous surfactant solution was injected into the cell kept at the desired temperature for the measurement. Afterwards, the cell was filled with 45 ml of CO_2 and the pressure was adjusted to the desired value. Once the cell was filled, the pressure was kept constant by using a computer-controlled pump connected to the hydraulic side of the cell. The cell was tilted 50° - 60° to increase the contact area between the phases. Then the system was left under static conditions for 24 h.

After 24 h, a sample of approximately 6 - 8 ml of aqueous phase was extracted at a low rate, keeping constant pressure inside the cell by moving the cell piston (assisted by the computer-controlled system). Before collecting the sample, approximately 2 ml of sample were discarded. During the extraction process, the system in the cell never exceeded 2 bar deviation from the target pressure. The extracted sample was collected for further analysis.

3.3. Surfactant Analysis

The surfactant concentration in SSW was determined by HPLC using a LC-4A HPLC from Shimadzu. The oven (Shimadzu CTO-2AS) was set at 50°C. The column used was a Supelcosil LC-18 (250 mm – 4.6 mm, 5 µm) and the samples were injected through a Rheodyne 7125 injector with a 20 µl loop. A refractive index detector from Showa Denko K.K (RI SE-51) was used to detect the peaks. The chromatograms were processed with the PowerChrom 180R system from eDAQ.

The eluent was prepared from measured amounts of methanol (HPLC grade from VWR) and water (obtained from a purification system PURELAB-Option Q DV-25). The methanol:water volume ratio used was 85:15 and the eluent had a concentration of 0.2 M $NaNO_3$ (analysis grade from Merck). The eluent was filtrated through a 0.45 µm nylon membrane and continuously degassed with helium.

3.4. Determination of partition coefficient

The partition coefficient, k_p, is determined by the expression in Eq. 1.

$$k_p = \frac{\frac{m_{sCO_2}}{m_{sCO_2} + m_{CO_2}}}{\frac{m_{sw}}{m_{sw} + m_w}} \quad (1)$$

where, m_{sCO_2} is the mass of surfactant dissolved in CO_2, m_{CO_2} the mass of CO_2, m_{sw} the mass of surfactant dissolved in the aqueous phase, and m_w the mass of aqueous phase. The solubility of water in CO_2 and CO_2 in water were neglected.

Some initial tests were done with surfactant dissolved in distilled water (0.5 wt.%) and CO_2. The total volume was 60 ml (15 ml aqueous phase, 45 ml of CO_2) and the experiments were carried at room temperature and 100 bar. In these tests, the aqueous samples were obtained as detailed above. Afterwards, a large and known volume of CO_2 was extracted from the cell and flashed to ambient pressure at a very low rate. The cell pressure was constant at 100 bar. The CO_2 extracted from the cell was passed through a water trap. After the flash, the flow line from the cell to the trap was washed with

water. With known total masses of water and extracted CO_2 HPLC analysis of the water enabled the determination of m_{sCO_2}. Then, m_{sCO_2} determined by HPLC was compared to m_{sCO_2} determined by mass balance based on m_{sw} (Table 2).

Table 2. Surfactant masses and partition coefficients determined by analysing both phases (HPLC) and only aqueous phase (M.B.) for pure water/CO_2 systems at room temperature and 100 bar.

Surfactant	M.B. m_{sCO_2} [g]	HPLC m_{sCO_2} [g]	M.B. k_p	HPLC k_p
Tergitol 15-S-9 (1)	0.031	0.031	0.28	0.28
Tergitol 15-S-9 (2)	0.034	0.029	0.33	0.28
Tergitol TMN 10 (1)	0.028	0.026	0.23	0.23
Tergitol TMN 10 (2)	0.028	0.029	0.23	0.22

The two methods for determining the surfactant mass dissolved in CO_2 and the partition coefficient gave same results. Thus, it was decided to proceed by only analysing the aqueous phase and determine m_{sCO_2} from the surfactant mass balance. In this manner the measurements could be performed more rapidly.

In order to ensure that the systems were in equilibrium at the time of sampling, a series of sampling tests were performed to determine the equilibration time required. It was observed that 20 h were enough for the systems to have unalterable concentrations of surfactant in both phases, so it was decided that all systems would age 24 h in the cell to ensure equilibrium.

4. Results

4.1. Cloud point determination

The cloud points for the surfactants used are shown in Table 3. For Brij L23 was not possible to determine the cloud point due to its high value (above 100°C). The solution of 0.5 wt.% Brij C10 in SSW was already cloudy at room temperature. This was unexpected since it is specified to be above 50°C (1 wt.% in water) from its producer. This surfactant was discarded for further measurements.

Table 3. Measured cloud points in SSW (0.5 wt.%).

Surfactant	Cloud Point [°C]
Tergitol 15-S-9	50
Tergitol NP 10	55
Tergitol TMN 10	70
Igepal CO 720	75
Igepal CA 720	80
Brij L23	> 92

4.2. Partition coefficients

Determination of partition coefficients was carried out at pressures of 100, 200, and 300 bar, and at room temperature, 40°C, and 80°C. The room temperature was typically around 20 – 22°C but is hereafter referred to as 20°C. All measurements were repeated at least twice. The error bars in the figures show the standard deviation for each experimental condition.

4.2.1. Linear alkyl ethoxylates

Brij L23

Brij L23 showed low CO_2 solubility at room temperature and at 40°C. Figure 2 depicts the surfactant distribution in each phase for the studied conditions. More than the 90 wt.% of the surfactant remained in the SSW at temperatures of 20°C and 40°C. However, the surfactant content in CO_2 increased significantly at pressures of 200 and 300 bar when the temperature was increased to 80°C. It can be

observed how the 85 wt.% of the surfactant migrated towards the CO_2 phase when the pressure was 200 bar. At 300 bar, the 93 wt.% was found solubilized in the CO_2 phase.

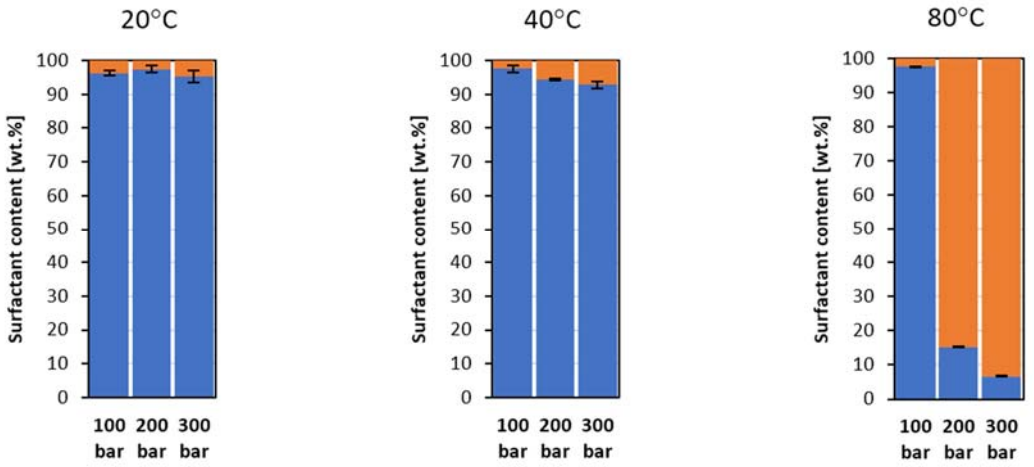

Figure 2. Surfactant distribution in SSW (blue) and in CO_2 (orange) for Brij L23.

Figure 3 depicts the partition coefficients, the surfactant concentrations in SSW, and the surfactant concentration in CO_2. At room temperature, the variation of the partition coefficient with pressure was almost negligible. At 40°C, a trend to increase the partition coefficient with increasing temperature was seen. A significant pressure effect on the partition coefficient was observed at 80°C. Note that the scale of the partition coefficients varies in Figure 3 and the following figures.

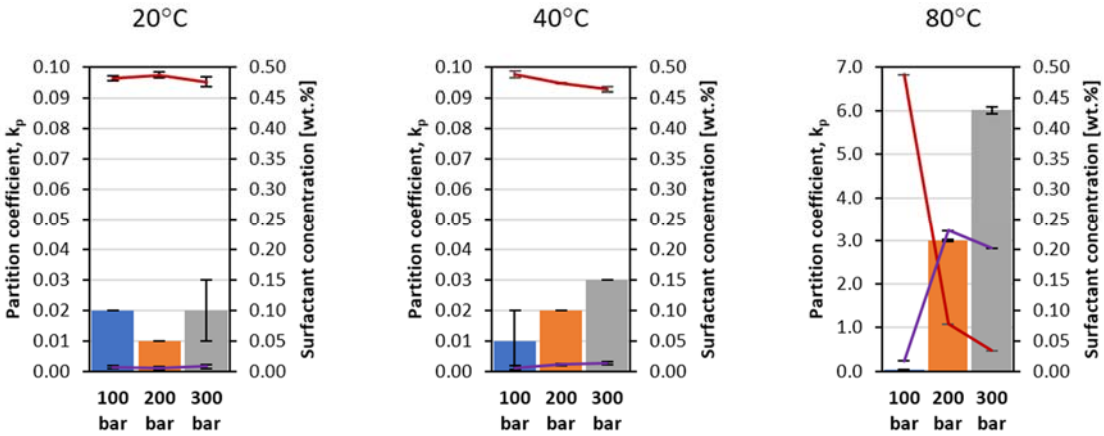

Figure 3. Partition coefficients for Brij L23 (bars). In red line, surfactant concentration in SSW; in purple, surfactant concentration in CO_2.

The concentration of surfactant decreased in SSW and increased in CO_2 as the partition coefficient was increased. However, at 80°C, this trend was not followed for the surfactant concentration in CO_2 for pressures of 200 and 300 bar. The decrease in concentration was due to the constant volume condition during the measurements. At 300 bar, 45 ml of CO_2 corresponds to 33.9 g CO_2 (0.746 g/ml) while, at 200 bar, the mass of 45 ml CO_2 was 26.8 g (0.594 g/ml). The mass of surfactant solubilized into the CO_2 was, therefore, larger at 300 bar (0.069 g) compared to 200 bar (0.062 g). The increase of the CO_2 mass when the system was at 300 bar, translates into a lower surfactant concentration.

4.2.2. Branched alkyl ethoxylates

Tergitol 15-S-9

Of all surfactants studied in this work, Tergitol 15-S-9 showed the highest partition in CO_2 at room temperature. At 100 bar, 47 wt.% of the surfactant solubilized into the CO_2 (Figure 4). A temperature increase from 20°C to 40°C did not promote any significant variation. When the temperature was increased further approaching the cloud point (2°C below), a significant solubility increase in the CO_2 phase was observed. Increased pressure increased the surfactant preference for the CO_2 phase. Both at 200 bar and 300 bar the partition towards the CO_2 phase increased significantly with increased temperature. At 300 bar and 48°C, only 0.9 wt.% of the surfactant remained in SSW.

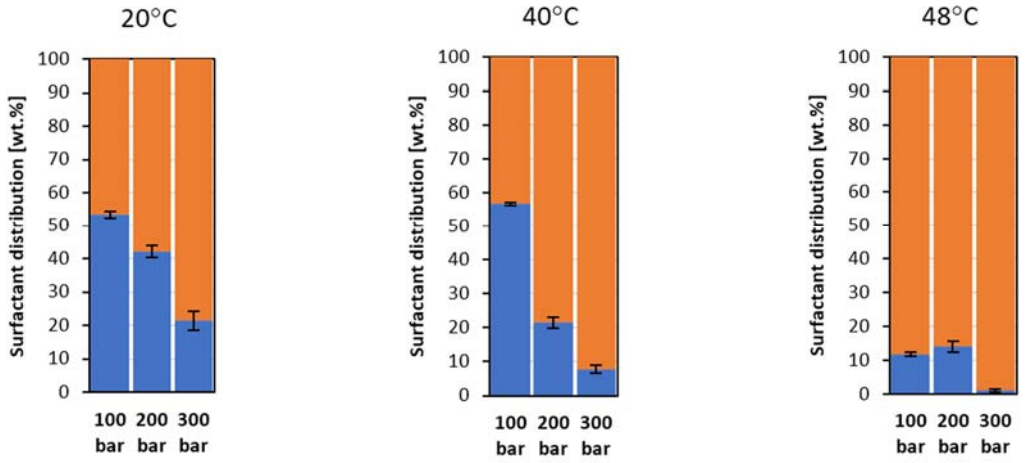

Figure 4. Surfactant distribution in SSW (blue) and in CO_2 (orange) for Tergitol 15-S-9.

The partition coefficient increased as temperature and pressure increased (Figure 5). At 48°C, no significant variation of the surfactant concentration in SSW was observed at 100 bar and 200 bar. However, a significant decrease in the surfactant concentration in the CO_2 was observed at these conditions. This decrease was partly a consequence of density effects, as explained before. As seen in Figure 4, the surfactant content in the CO_2 phase decreased from 88 wt.% (100 bar) to 86 wt.% (200 bar). Due to the mentioned effect, the decrease in the concentration was from 0.34 wt.% to 0.18 wt.%.

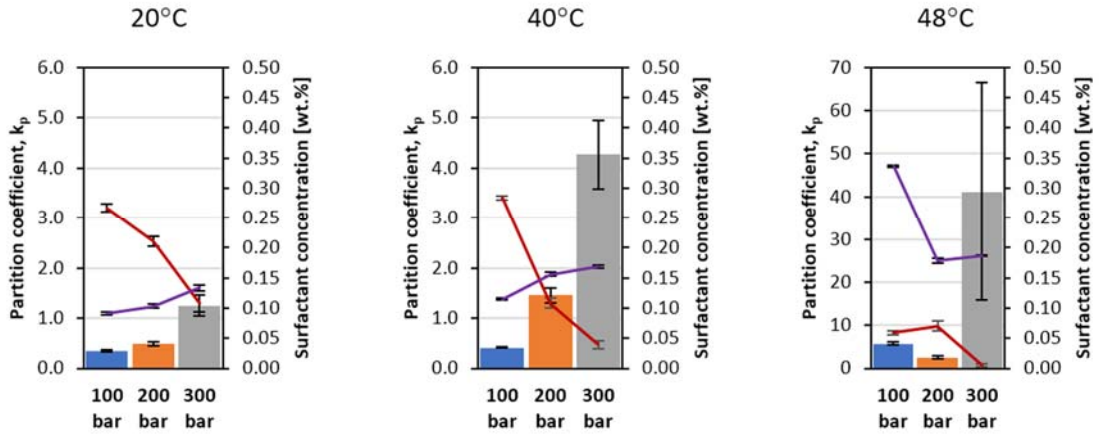

Figure 5. Partition coefficients for Tergitol 15-S-9 (bars). In red line, surfactant concentration in SSW; in purple, surfactant concentration in CO_2.

Tergitol TMN 10

Tergitol TMN 10 also exhibited a preference for the CO_2 phase. The surfactant solubility in the CO_2 phase increased with pressure (Figure 6). Increased temperature also promoted surfactant partitioning towards the CO_2 phase except at 100 bar when the temperature was increased from 20°C to 40°C where the surfactant content in the CO_2 decreased from 39 wt.% to 16 wt.%. At 69°C, the residual surfactant in SSW decreased to 2.6 wt.%, 2.1 wt.% and 1.3 wt.% at 100 bar, 200 bar and 300 bar, respectively. Tergitol TMN 10 was highly CO_2-philic at this temperature.

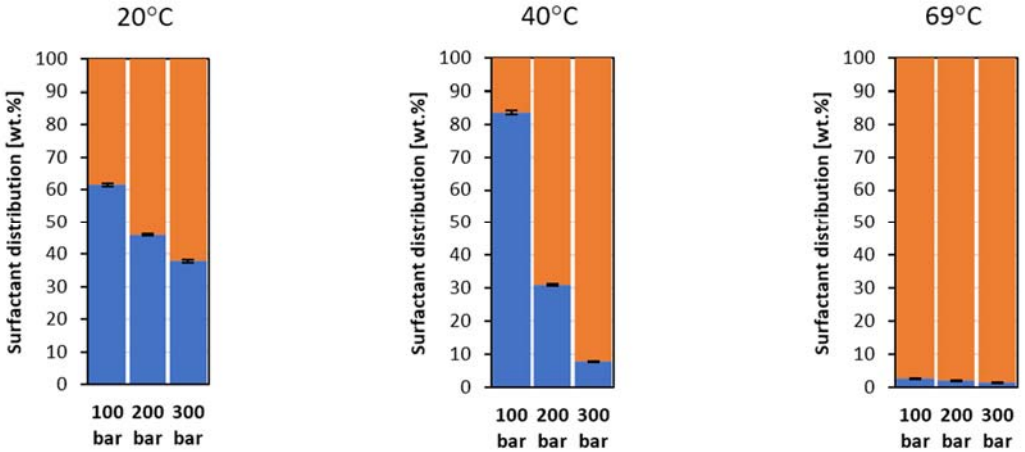

Figure 6. Surfactant distribution in SSW (blue) and CO_2 (orange) for Tergitol TMN 10.

The partition coefficient increased as pressure increased for 20°C and 40°C (Figure 7). However, at 100 bar the partition coefficient decreased when the temperature increased from 20°C to 40°C. At 69°C, a deviation from this trend was observed. The highest coefficient was obtained at 100 bar. When the pressure was increased to 200 bar, the coefficient decreased significantly. A further increase of pressure to 300 bar resulted in an increased partition coefficient. The surfactant concentration in the CO_2 phase decreased. Meanwhile, the surfactant content in the same phase increased (Figure 7 and Figure 6). This observation is explained by the density effect as explained previously.

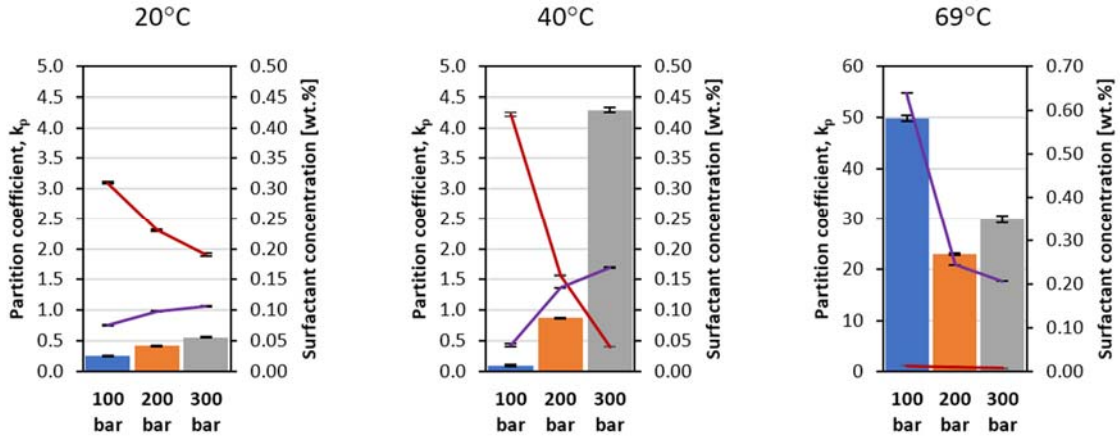

Figure 7. Partition coefficient for Tergitol TMN 10 (bars). In red line, residual surfactant concentration in SSW; in purple, surfactant concentration in CO_2.

4.2.3. Linear alkylphenol ethoxylates

Igepal CO 720

The preference of Igepal CO 720 for the CO_2 phase generally increased as both temperature and pressure increased (Figure 8). One exception was observed at 100 bar, however. When the temperature increased from 20°C to 40°C the surfactant content in the CO_2 phase decreased. This surfactant had preference for the CO_2 phase as the temperature approached its cloud point (75°C, see Table 3). At this temperature, the content of surfactant in SSW was 3.0 wt.%, 0.8 wt.%, and 0.4 wt.% at pressures of 100 bar, 200 bar, and 300 bar, respectively.

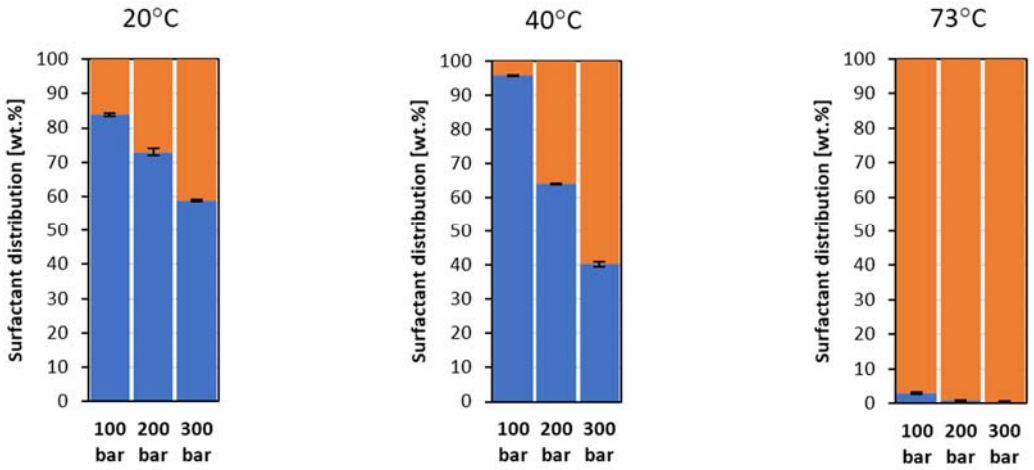

Figure 8. Surfactant distribution in SSW (blue) and in CO_2 (orange) for Igepal CO 720.

The partition coefficient followed the expected trend, it increased with temperature and pressure (Figure 9). The same exception was observed at 100 bar at temperatures of 20°C and 40°C, where the partitioning coefficient decreased for increasing temperature.

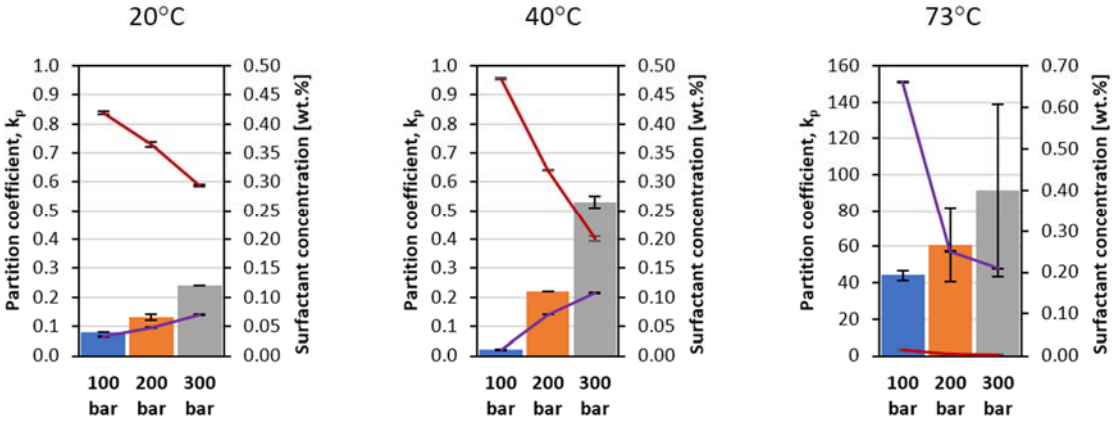

Figure 9. Partition coefficient for Igepal CO 720 (bars). In red line, residual surfactant concentration in SSW; in purple, surfactant concentration in CO_2.

4.2.4. Branched alkylphenol ethoxylates

Igepal CA 720

Igepal CA 720 showed similar surfactant distributions as Igepal CO 720. The same observations at 100 bar and 40°C were made (Figure 10) as the preference for the CO_2 phase decreased compared to 20°C. At 78°C, most of the surfactant was dissolved in the CO_2, 97.8 wt.% (100 bar), 98.2 wt.% (200 bar), and 98.9 wt.% (300 bar).

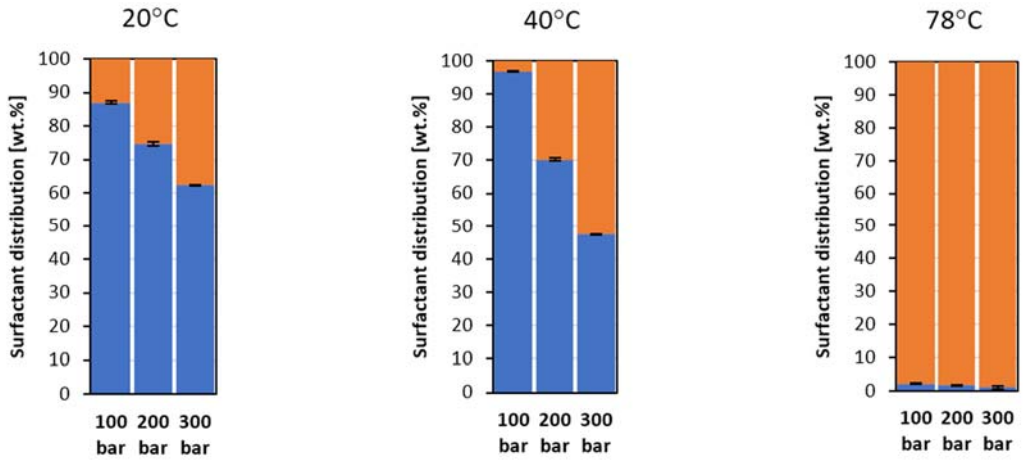

Figure 10. Surfactant distribution in SSW (blue) and in CO_2 (orange) for Igepal CA 720.

The partition coefficient followed the expected trend at 20°C and 40°C. It increased as both temperature and pressure increased with the exception of 100 bar (Figure 11). At 78°C, the partitioning coefficient decreased when the pressure was increased from 100 bar to 200 bar. The reduced partitioning coefficient, as well as the diminishing concentration in the CO_2 phase, is caused by the density effect explained previously.

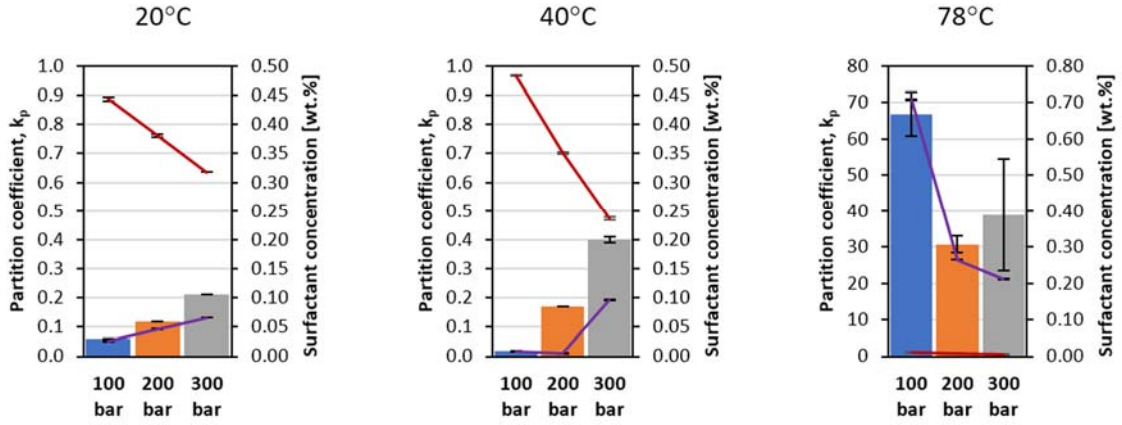

Figure 11. Partition coefficient for Igepal CA 720 (bars). In red line, residual surfactant concentration in SSW; in purple, surfactant concentration in CO_2.

Tergitol NP 10

Tergitol NP 10 did not follow any clear trend in its distribution between CO_2 and SSW (Figure 12). At 20°C, the preference for the CO_2 phase increased as the pressure was increased. At 40°C, the CO_2 distribution was higher 100 bar, lower for 200 bar, and higher for 300 bar, compared to 20°C. The lowest

content in CO_2 was observed at 40°C and 200 bar where only 20 wt.% of the total surfactant was solubilized in the CO_2 phase. The largest content of surfactant in CO_2 was at 53.7°C both for 200 bar and 300 bar, where approximately 60 wt.% of the surfactant was in the CO_2 phase.

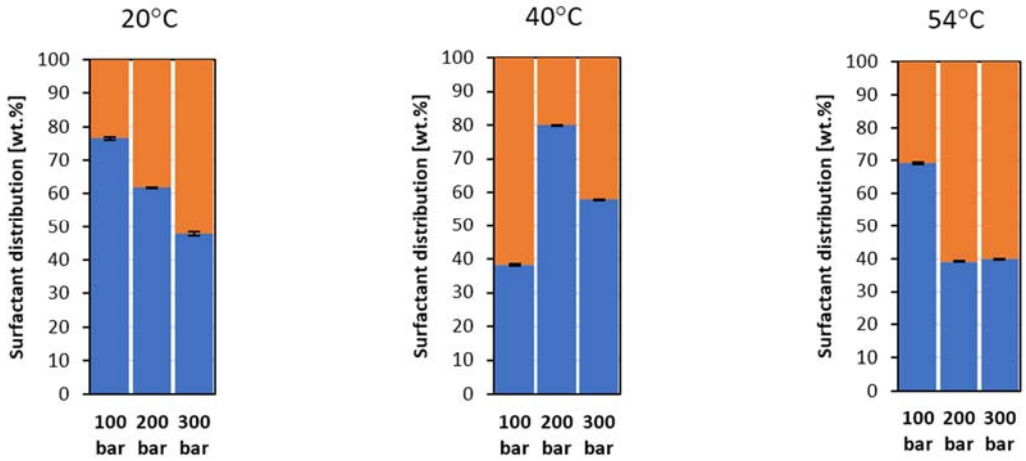

Figure 12. Surfactant distribution in SSW (blue) and in CO_2 (orange) for Tergitol NP 10.

At 20°C, the partition coefficient increased with pressure in accordance with the relative surfactant content. The largest coefficient was observed at 40°C and 100 bar (Figure 13). At 200 bar the coefficient decreased compared to 100 bar and increased when the pressure was increased to 300 bar. At 53.7°C, right below its cloud point, an opposite trend when compared to 40°C was observed. The coefficient increased from 100 to 200 bar and decreased again when the pressure was 300 bar.

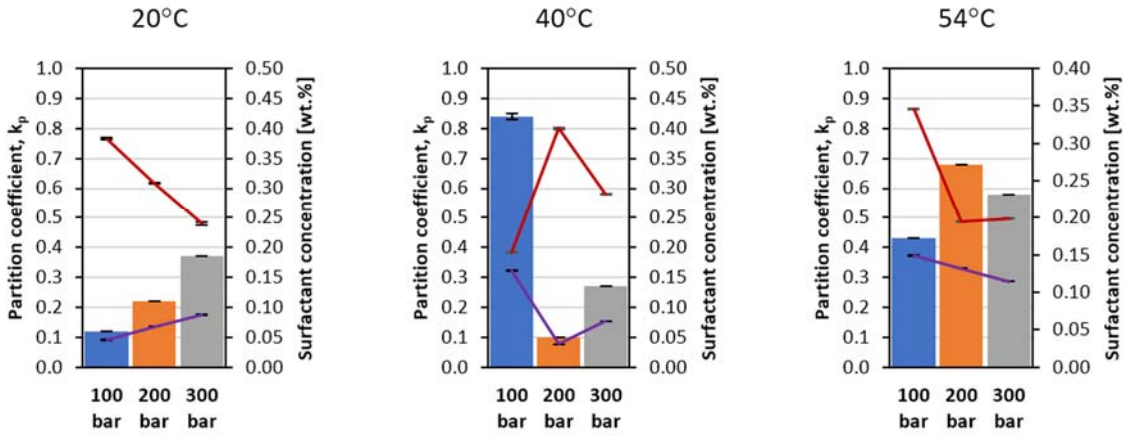

Figure 13. Partition coefficient for Tergitol NP 10 (bars). In red line, residual surfactant concentration in SSW; in purple, surfactant concentration in CO_2.

4.3. Effect of concentration on partitioning

The effect of surfactant concentration on the partitioning was also studied for two surfactants, Tergitol TMN 10 and Brij L23. The results are depicted in Figure 14. The concentrations plotted are the residual concentration in SSW after equilibration at 40°C. The pressures used were 100, 200, and 300 bar.

For both surfactants, the increase of pressure promoted partitioning towards the CO_2 phase. However, as the concentration of surfactant in SSW increased, the partition coefficients decreased until plateau

values were reached (Figure 14). At 100 bar the partition coefficient for Tergitol TMN 10 exhibited an almost constant value (Figure 14.a) seemingly unaffected by concentration.

The partitioning coefficients were fitted to the exponential functions of the form:

$$k_p = A + Be^{-C \cdot Conc} \tag{2}$$

where k_p is the partition coefficient, $Conc$ is the surfactant concentration in SSW expressed in wt.%, and A, B, and C are empirical constants determined by the least-squares non-linear regression (Table 4).

Table 4. Equation 4 empirical constants determined for Tergitol TMN 10 and Brij L23.

	Tergitol TMN 10				Brij L23		
	A	B	C		A	B	C
100 bar	0.1944	0.1390	4.3653	100 bar	0.0069	0.0518	5.7471
200 bar	0.2897	1.2740	4.3653	200 bar	0.0052	0.0439	2.2624
300 bar	0.5929	3.9281	5.9617	300 bar	0.0155	0.1054	4.3842

Figure 14 depicts the partition coefficient as a function of the surfactant concentration in SSW at equilibrium. The model gives a fair fit for all measurements.

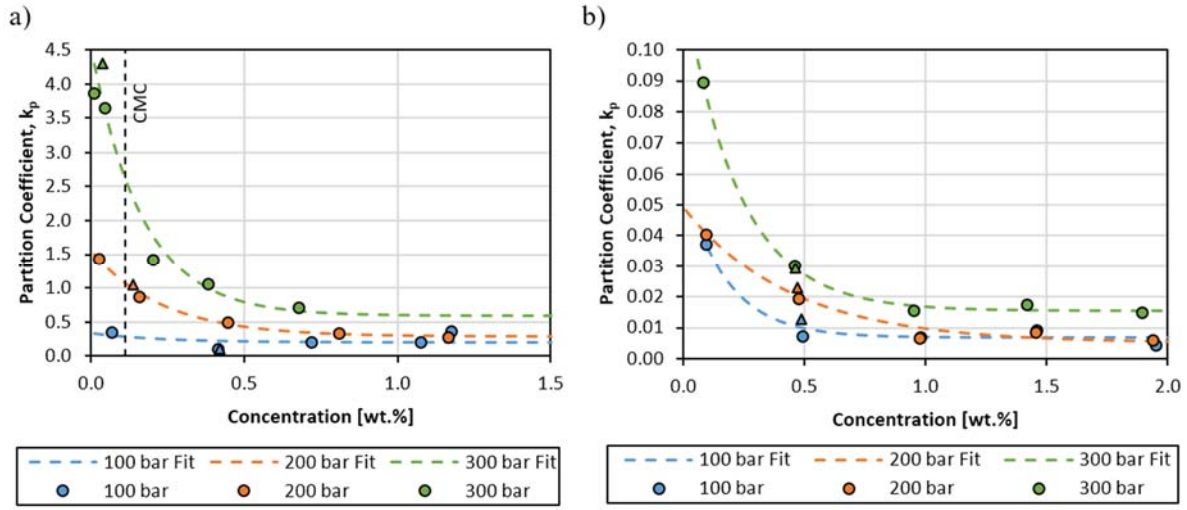

Figure 14. Partition coefficient as a function of surfactant concentration at 40°C for a) Tergitol TMN 10 (CMC_{aq} = 0.11 wt.%) and b) Brij L23 (CMC_{aq} = 0.01 wt.%). The data points marked with triangles correspond to a separate set of measurements.

5. Discussion

The surfactants selected for this research can be classified into two groups, alkyl ethoxylates and alkylphenol ethoxylates. Each group have similar ethoxylation numbers (except Brij L23) with carbon tails varying from linear to more branched structures. Nonetheless, a small variation on the CO_2-philic moiety can have an important impact on the partition between aqueous and CO_2 phase. Also, some trends can be identified. One constant observation in all measurements (excepting Tergitol NP 10) was a decrease in the CO_2 solubility as temperature increased from 20°C to 40°C at 100 bar.

5.1. Alkyl ethoxylates

The partition in CO_2 was generally promoted as the degree of branching increased for the alkyl ethoxylates. However, at temperatures up to 40°C, highly branched carbon chains could cause a solubility decrease in CO_2. This could be explained by an increase in the "stiffness" of the CO_2-philic moiety. Thus, as the solubility increases by the effect of increasing the methyl branching, it is counteracted by a decrease of its conformational entropy, according to Flory and Huggins (Flory, 1953). Above 40°C, Tergitol TMN 10 obtained a larger preference for the CO_2 phase than Tergitol 15-S-9. However, the highest temperatures studied were not the same for both surfactants as the highest temperature measured for each surfactant is limited by their cloud point.

Brij L23, the highly hydrophilic non-branched linear alkyl ethoxylate, the partitioning decreased as temperature increased for 100 bar. This observation is in agreement with the research reported by Chen *et al.* for similar surfactants at 117 bar for 24 and 40°C (Chen *et al.*, 2015). They explained it as a lowered solvent strength of CO_2, which reflected a lowered tail solvation due to the decrease of density and a weakened hydrogen bonding between the head groups due to the temperature increase. However, the opposite trend was observed at pressures of 200 and 300 bar for increasing temperature. Here, as CO_2 density decreased with increasing temperature, the surfactant solubility in CO_2 increased. Thus, this observation cannot be explained by the lowered solvent strength and decreased tail solvation in CO_2. A plausible explanation for the increased partitioning is that as solubility in the aqueous phase is decreased with increasing temperature, surfactant partitions to the CO_2 phase and eventually starts forming micelles. Thus, even if tail solvation in CO_2 is reduced, surfactant partitions to the CO_2 and increases the micelle concentration.

A similar observation was made for Tergitol TMN 10 at 100 bar, where partition coefficient decreased as temperature increased from 20 to 40°C. However, a further increase of temperature to 69°C, just below systems cloud point, drastically increased the coefficient. Close to the cloud point, the weakened hydrogen bonding between ethoxy-groups and water would favour surfactant migration towards CO_2.

5.2. Alkylphenol ethoxylates

Generally, increased pressure and temperature contributed to larger partition coefficients also for the alkylphenol ethoxylates. At 100 bar, when the temperature was increased from 20°C to 40°C, the same decrease in the partition coefficient observed with alkyl ethoxylates was also noticed.

Both Igepal CO 720 and Igepal CA 720 had similar solubilities into the CO_2, meaning that high ramification of the CO_2-philic moiety did not have a major effect on their partition. Igepal CO 720 is a linear alkylphenol ethoxylate with 9 carbons on its hydrophobic tail. Igepal CA 720 contains 8 carbons but arranged in a highly ramified structure as it can be seen from Figure 1. It is also possible that the aromatic ring in the CO_2-philic moiety influenced the partitioning. From the comparison between alkyl ethoxylates and alkylphenol ethoxylates, it is observed that the presence of a benzene ring in the CO_2-philic moiety has a slight detriment on its solubility and partitioning into CO_2 when temperatures were not close to their respective cloud point.

For both surfactants, a decrease in the partition coefficient was observed at 100 bar when the temperature was increased from 20 to 40°C. Further increase of temperature increased the coefficient, the same observation noticed for the branched alkyl ethoxylates. The variations on the partitioning as pressure and temperature are varied can only be explained by the balance between tail solvation in CO_2, micellization in CO_2, and strength variation of the hydrogen bond interactions between water molecules and hydrophilic headgroups.

Tergitol NP 10 can be considered as a medium branched alkylphenol ethoxylate. This surfactant did not follow apparently any specific trend. When the temperature was increased from 20 to 40°C the partition coefficients at 200 and 300 bar were reduced, while it increased for 100 bar. At 53°C, the effect was the opposite; the partition coefficients increased at 200 and 300 bar but decreased at 100 bar (Figure 13).

Compared to the other alkylphenol ethoxylates, Tergitol NP 10 had a low partition coefficient even when the temperature was 2°C below its cloud point. For all studied conditions, the partition coefficient never was above 1, obtaining the largest partition at 53.7°C and 200 bar (k_p = 0.68). Hence, Tergitol NP 10 was the surfactant with the lowest observed CO_2 solubility in the study, the very hydrophilic Brij L23 excluded. According to the conformational entropy approach, this surfactant should have obtained the largest CO_2 solubility among the studied alkylphenol ethoxylates. However, this was the case only for the measurements at 20°C and the measurement of 100 bar at 40°C, where the partition coefficient was larger. Thus, the partitioning behaviour of this surfactant could not be properly explained.

5.3. Effect of concentration on partitioning

In an ideal system, chemical components should have concentration-independent partition coefficients, but for surfactants, there is a strong concentration dependence. Harusawa *et al*. studied the distribution of octylphenol ethoxylates with different ethoxylation between isooctane and water system (Harusawa *et al.*, 1980). For high ethoxylation numbers (EO 6 and 8) the surfactant concentration in the oil increased up to the CMC and then remained constant for higher surfactant concentrations in the water. For a low ethoxylation number (EO 4) the surfactant in the water phase remained constant after the CMC was reached, whereas the concentration in the oil increased. This indicated that micelles were formed in the oil phase. For an intermediate ethoxylation number (EO 5), the concentrations in both phases remained constant after the CMC was reached and a separate surfactant-rich phase was formed. Similar behaviour with constant concentrations in the oil phase (EO 6) or water phase (EO 8) after reaching the CMC was observed in a system composed by water and cyclohexane using nonylphenol ethoxylates (Harusawa *et al.*, 1980; Harusawa and Tanaka, 1981).

The systems studied in this work exhibited different behaviour. The continuous increase of the surfactant concentration in the CO_2 phase beyond their respective CMCs, as it can be seen in Figure 15, has already been observed and discussed (Balcan and Anghel, 2005). They noticed a slope change of the partition isotherm at the CMC studying systems composed of n-hexane, water, and a commercial nonylphenol ethoxylate with an average EO number of 10 as a surfactant. This behaviour resembles the one from surfactant mixtures, where the partitioning increases beyond the CMC (Cowell *et al.*, 2000; Harusawa *et al.*, 1982; Harusawa and Tanaka, 1981; Warr *et al.*, 1983). Commercial surfactants are molecules with the same CO_2-philic moiety but with polydisperse EO numbers. Thus, they are surfactant mixtures with dissimilar hydrophilic-lipophilic properties. After equilibration, the ethoxymer distribution was measured in both phases and they observed that the aqueous phase contained larger mean EO numbers than the n-hexane phase.

In the present study, the amount of surfactant in the CO_2 increased with an increased concentration in the brine, as it can be observed in Figure 15. The CMCs of Tergitol TMN 10 and Brij L23 in water are 0.11 wt.% and 0.01 wt.%, respectively (given by the provider). These results are consistent with previous observations (Balcan and Anghel, 2005) and with the theoretical partition model of polydisperse ethoxylated surfactants.

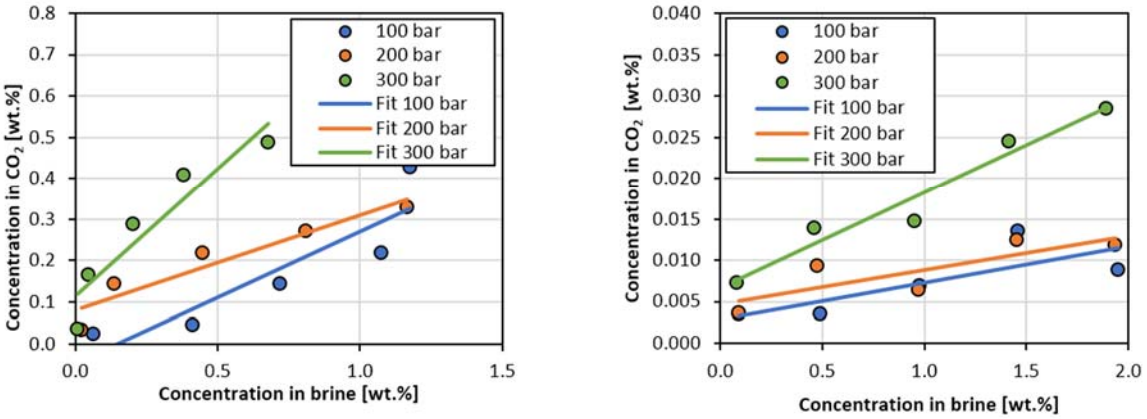

Figure 15. Equilibrium surfactant concentrations in CO_2 and SSW for Tergitol TMN 10 (left) and Brij L23 (right).

6. Conclusions

The effects of branching, temperature, and pressure on the partitioning of non-ionic surfactants for SSW-CO_2 systems have been studied. Two main surfactant types were studied, alkyl and alkylphenol ethoxylates. Aside from Brij L23, all surfactants had a similar ethoxylation number. The effect of concentration on the partition coefficient was also studied for the surfactants Tergitol TMN 10 and Brij L23. For both surfactants, it was observed that the partition coefficient decreased with increasing surfactant concentration in the aqueous phase. The observations resemble the behaviour of surfactant mixtures as commercial surfactants have polydispersed EO numbers.

In general, alkyl ethoxylates showed a tendency of increased solubilization in CO_2 as both pressure and temperature increased. Branched alkyl ethoxylates (Tergitol 15-S-9 and Tergitol TMN 10) showed the largest solubilization in CO_2 at low temperature and pressure. At 100 bar and 20°C, 53 wt.% and 62 wt.% of the surfactants solubilised in the CO_2, respectively. Brij L23, which is a linear alkyl ethoxylate with an ethoxylation number of 23, exhibited low solubilization up to 40°C. However, at 80°C most of the surfactant solubilized in the CO_2 when the system was pressurized to 200 bar and 300 bar. This observation was explained by the competitive effect between different mechanisms such as micellization in the CO_2, tail solvation in CO_2, and hydrogen bonding between ethoxylate groups and water molecules. Ramification increase of the hydrophobic tail is beneficial to increase CO_2 solubility to a certain degree for alkyl ethoxylates. Highly ramified tails might be detrimental possibly due to an increase of conformational entropy.

Alkylphenol ethoxylates showed lower solubilization than branched alkyl ethoxylates at 20°C and 40°C. However, high solubilisation in CO_2 was obtained both for Igepal CO 720 and Igepal CA 720 when the temperature was 2°C below their respective cloud points. The increase in solubilisation can possibly also be attributed to favourable interactions between ethoxylate groups and CO_2 as the hydrogen bonding with water molecules becomes weakened. Igepal CA 720 (branched alkylphenol moiety) obtained lower partition coefficients than Igepal CO 720 (linear alkylphenol moiety). This difference could be explained from the diminished conformational entropy that a more branched structure would have. No clear trend of tail ramification effect on CO_2 solubilization was identified for alkylphenol ethoxylates.

Acknowledgement: We acknowledge the Research Council of Norway for funding this work.

Author Contributions: The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding: The present work was done as part of the project "Improved performance of CO_2 EOR and underground storage by mobility control of CO_2" financed by the Research Council of Norway through the Climit Programme (Grant number 267859).

Conflicts of Interest: The authors declare no conflicts of interest.

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